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13. ABSTRACT *(Maximum 200 words)*

One-dimensional photonic materials with applications to optical limiting and optical switching have been developed in conjunction with the Naval Research Laboratory. This was accomplished by synergistically combining nanolayer coextrusion methodology with dispersion of nonlinear dyes and careful control of nanolayer refractive indices.

Novel ultrathin nanolayered polymers were created with layer thicknesses less than the radius of gyration of the macromolecule. Under these constrained conditions, crystalline layers approximately 11 nm thick were produced with two-dimensional hierarchical structures. By inclusion of gold or graphite nanoparticles, systems with novel electro-optical characteristics can be developed.

High barrier, injection moldable systems have been produced by microlayering a polymer with good water barrier and a polymer with good oxygen barrier. Taking advantage of differences in melting points, layer integrity was maintained during injection molding in between the two melting points. This concept, which utilizes and maintains the large interfacial surface area achieved with microlayering, is broadly applicable to highly immiscible polymeric systems.

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ENCLOSURE 1

New Microlayer and Nanolayer Polymer Composites

DAAG55-98-1-0311

Interim Report, 1/1/00-12/31/00

By

Eric Baer and Anne Hiltner

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Abstract

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Publications

Effect of Strain on the Properties of an Ethylene-Octene Elastomer with Conductive Carbon Fillers, by L. Flandin, A. Chang, S. Nazarenko, A. Hiltner and E. Baer, J. Appl. Polym. Sci., **76**, 894-905 (2000).

Comparison of Irreversible Deformation and Yielding in Microlayers of PC with PMMA and SAN, by J. Kerns, A. Hsieh, A. Hiltner and E. Baer, J. Appl. Polym. Sci., **77**, 1545-1557 (2000).

Processing and Properties of Polymer Microlayered Systems, by E. Baer, J. Kerns and A. Hiltner, in *Structure Development during Polymer Processing* (A. M. Cunha and S. Fakirov, eds.), NATO Science Series, Series E: Applied Sciences, Vol. 370, Kluwer, 2000. pp 327-344.

Interrelationships between Electrical and mechanical Properties of a Carbon Black-Filled Ethfylene-octene Elastomer, by L. Flandin, A. Hiltner and E. Baer, Polymer, **42**, 827-838 (2001).

Presentations by PI

Invited lecturer on "Polymer Micro and Nano-Layered Composites," Roger S. Porter Memorial Symposium, Asilomar Conference Grounds, Pacific Grove, California, February 4-6, 2000.

Invited lecturer on "New Micro and Nanolayered Polymer Systems," World Polymer Congress (IUPAC MACRO 2000), Warsaw, Poland, July 13, 2000.

Invited lecturer on "Polymer Microlayer Composites," Centre of Molecular & Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland, July 19, 2000.

Invited Keynote address lecturer on "Nano and Microlayered Polymers: Processing, Structure and Properties," European Physical Society, Guimaraes, Portugal, September 25-28, 2000.

Invited lecturer on "Polymer Microlayered Composites," The Case School of Engineering, A.W. Smith Building, Room 329, November 30, 2000.

Invited lecturer on "Polymer Microlayer Coextrusion and Composites," Eveready Battery Company, Westlake, Ohio, December 13, 2000.

Invited lecturer on "Microlayering as a Route to Designed Polymer Alloys," Pacifichem 2000 Symposium, Honolulu, Hawaii, December 14-19, 2000.

Personnel

Faculty: E. Baer, A. Hiltner

Research Associates: L. Flandin, M. Roganova, E. V. Stepanov, L. Zhang

Graduate Students: J. Kerns, M. Hahn

Awards and Honors

Eric Baer was inducted in the Plastics Hall of Fame

Anne Hiltner received the Cooperative Research Award from the American Chemical Society

Interactions with Army Personnel

Created concept for microlayered and nanolayered materials for application in optical limiting and laser protection with Dr. James Shirk (NRL), processed microlayered materials and supplied them to the Naval Research Laboratories for testing. Resulted in patent disclosure and submission of abstracts to three national meetings: ACS spring 2001 meeting, MRS spring 2001 meeting, CLEO/QELS spring 2001 meeting.

Supplied microlayered materials to Triton, Inc. for ballistic studies directed by Dr. Alex Hsieh (ARL-Aberdeen).

Developed concepts for proposal on "Ballistic Resistance and Deformation of Microlayered Polymeric Materials Suitable for Face-Shield" with LtC Geoffrey A. Thompson and Col. Dennis A. Runyan (USArmy Dental Corp.).

Technology Transfer

Provisional patent application filed on "Polymer 1-D Photonic Crystals"

Inventors: E. Baer, A. Hiltner and J. Shirk

Abstract: The invention provides the materials and a method for fabricating multiplayer nonlinear dielectric optical structures from polymers. These materials are characterized by a modulation in the nonlinear refractive index in the direction normal to the surface of the layers. Such materials behave as 1-D photonic crystal material. They can perform a variety of nonlinear optical functions including all-optical switching and passive optical limiting. Prior to this invention, 1-D photonic crystal materials were generally small and fragile as well as difficult and expensive to fabricate. The polymeric nonlinear materials described here are flexible sheets with much larger dimensions than were available previously. Structures many feet wide and of any length can be economically produced.

Accomplishments

Nonlinear Nanolayered Polymers: 1D Photonic Materials with Applications to Optical Limiting

Large area, polymeric, 1D photonic crystal materials were fabricated by a nanolayer coextrusion technique. This method gives a layered polymer structure with thousands of layers and a layer thickness down to about 10 nm. We fabricated a series of nanolayered materials both with and without nonlinear dyes in alternate layers. The nanometer scale layers were demonstrated by AFM measurements. Further, a nanolayered sample with a small index difference between the layers had transmission and reflection properties consistent with a multilayer dielectric reflector with the distribution of layer thickness found in the AFM measurements. Alternate layers were then doped with a nonlinear dye to give a dielectric stack where the index difference between the layers is intensity dependent. Such nanostructured materials have several uses in optics and optoelectronics, including optical limiters for eye and sensor protection in the visible and near IR.

Nanolayered Crystalline Polymers

Under normal bulk crystallization conditions, polymers crystallize into three-dimensional hierarchical structures by nucleation and growth of lamellae to form spherulites. As the film thickness is decreased, the growth is limited in the third dimension at different hierarchical scales. Of interest here is the case of ultrathin polymer layers where the layer thickness is less than the polymer molecular radius of gyration. Under these constrained conditions, unexpected and novel phenomena can be expected. Using nanolayer extrusion, it is possible to achieve films where the layer thickness can be controlled at the nanoscale of the polymer molecules. Experiments have been performed on two polymer systems, both of which combine a crystalline polymer (polyethylene or polypropylene) with a glassy polymer (polystyrene).

In nanolayers of polypropylene, 3D spherulites are replaced by 2D discoids. The substructure of the discoids changes from close-packed lamellae to individual radial lamellae distributed in a granular matrix. The morphological change is accompanied by transformation of the crystal structure a mixture of α- and β-spherulites to a mesophase.

Processing of layered materials containing continuous polyethylene nanolayers 11 nm thick separated by polystyrene layers has been demonstrated. The molecular weight of the polyethylene used in the nanolayers has been optimized. The nanolayers can be made functional by incorporation of a filler particle, such as graphite or gold. Such nanostructured materials would be useful as sensors or for signal transmission.

High Barrier Materials from Microlayered Polymers

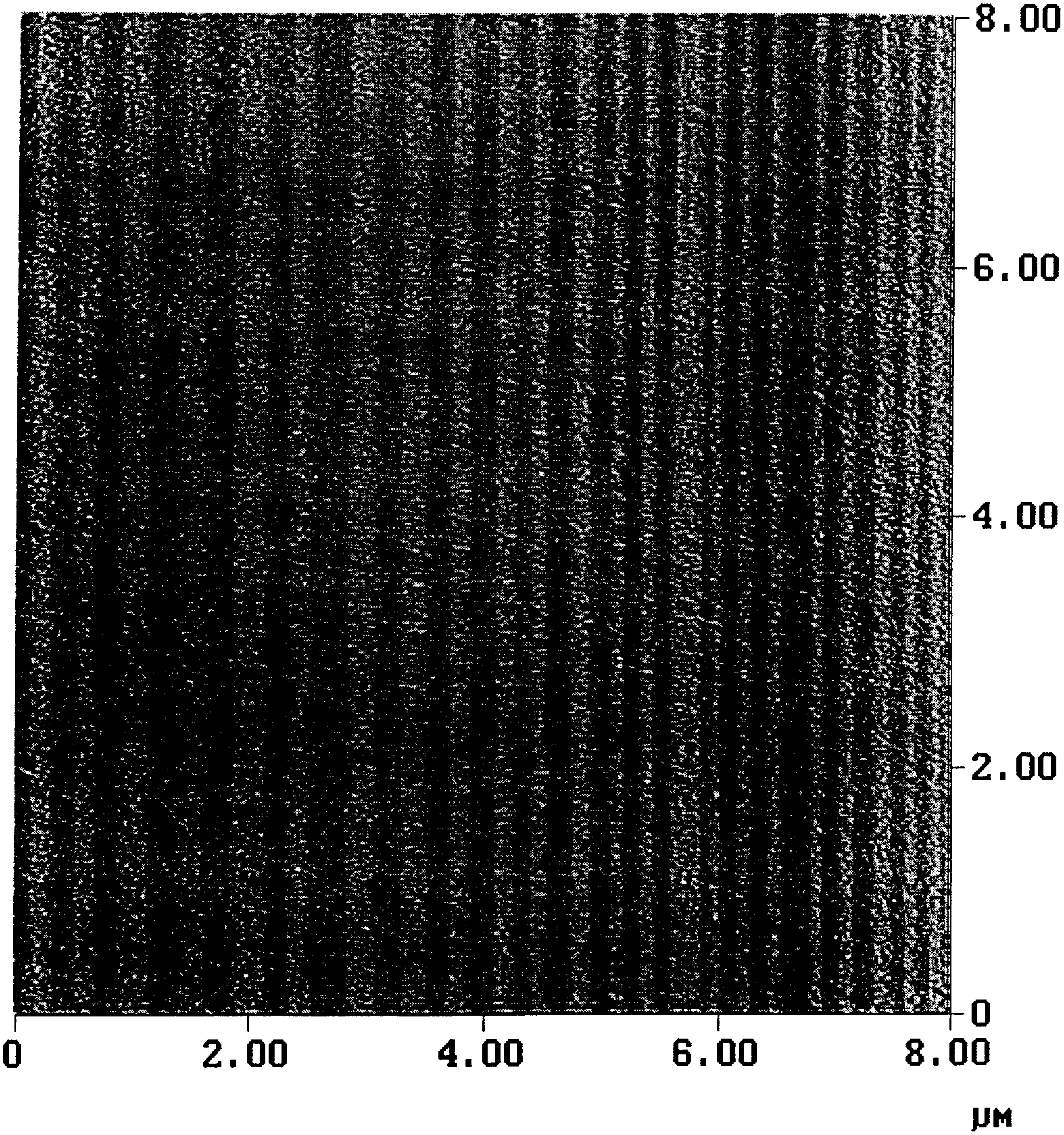
Nanolayer coextrusion can be used as a compounding method for obtaining a dispersion of very high aspect ratio nanoparticles in an injection molded polymer article. To demonstrate the concept, a polymer with good water barrier and good solvent resistance (polypropylene, PP) was microlayered with a polymer having excellent gas barrier (polyamide 66, PA66). Taking advantage of the large difference in melting points, the microlayer was injection molded at a temperature in between the melting points of PP (160°C) and PA66 (260°C). Layering of PA66 was retained in the finished article. Due to the high aspect ratio of the layers, the oxygen permeability was markedly reduced compared to a conventional injection molded article of the same composition.

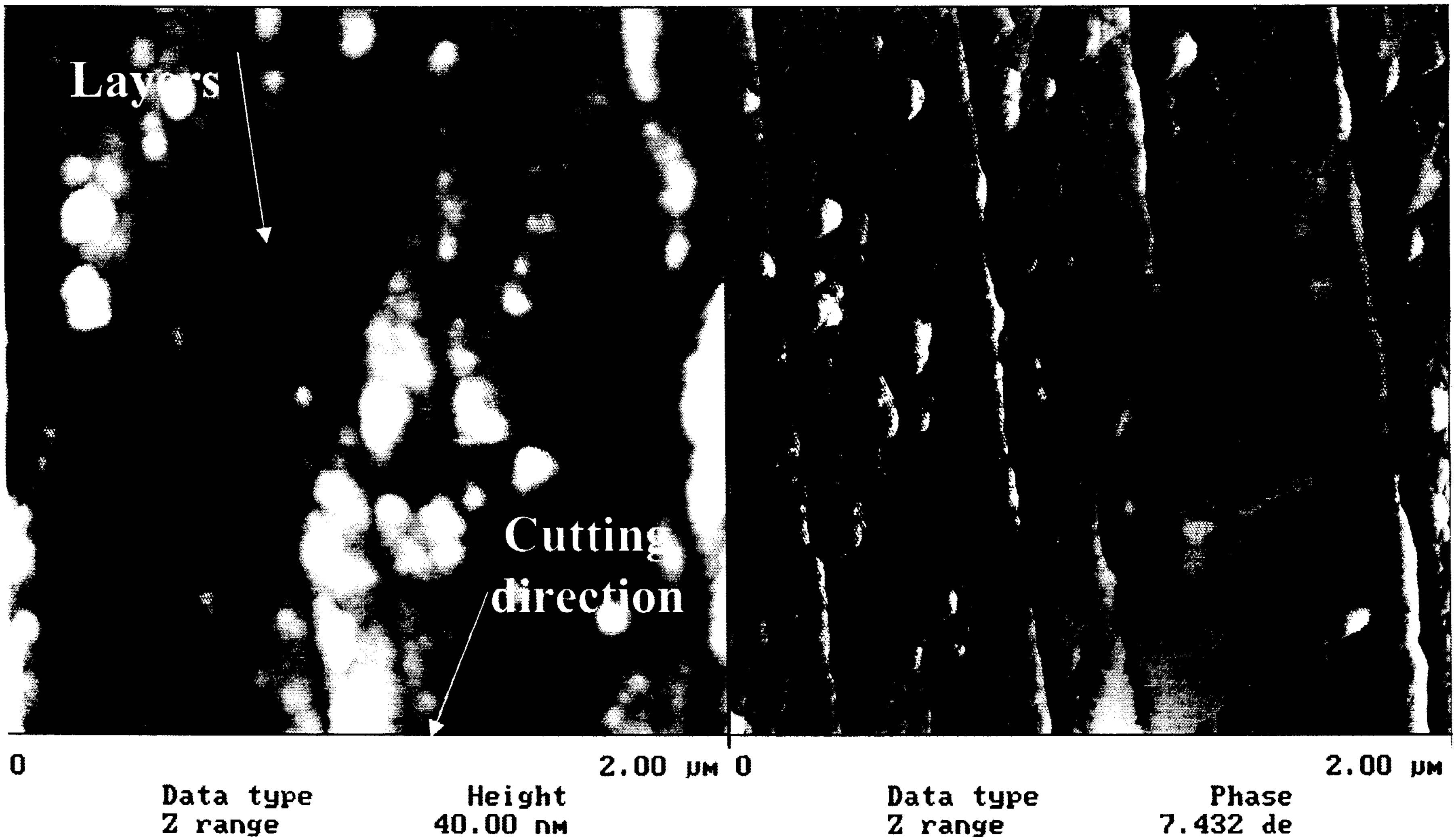
In one example (Table I), the microlayers consisted of 65% PP, 25% PA66 and 10% a modified polypropylene tie layer for good adhesion. Injection molding the microlayer below the melting temperature of PA66 resulted in a material with much lower permeability than the melt blend of the same composition. The permeability of the injection molded material was not as low as the microlayer due to the discontinuous nature of the layers after injection molding. (The oxygen barrier properties of the coextruded microlayer closely conformed to the series model for continuous layers whereas the melt blend was close to the parallel model). Good barrier of the injection molded microlayer was maintained over a broad processing window, 180-240°C. However, good barrier was lost if the layers melted, for example by injection molding at 280°C, above the melting temperature of PA66. The approach can be extended to many combinations of barrier materials. The concept is also applicable to modulus enhancement.

Table I. Oxygen Barrier Performance of Injection Molded Microlayers

Material	Molding Temperature (°C)	Oxygen Permeability (cc cm m^{-2} day^{-1} atm^{-1})
Polyamide-66	280	0.064 ± 0.003
Polypropylene	180	7.51 ± 0.06
Microlayer	NA	0.30 ± 0.03
Injection Molded Microlayer (257 layers)	180	0.96 ± 0.03
	240	1.00 ± 0.11
	280	3.97 ± 0.08
Melt Blend	280	4.45 ± 0.04
Parallel Model		5.64
Series Model		0.254

AFM Phase Image of Nanolayered SAN20/SAN25+Dye 4096 layers





AFM Height and Phase Images of HDPE Nanolayers in a HDPE/PS Layered Film. The size of a HDPE layer is about 50 nm.